

# Catalytic wet air oxidation of phenol in concurrent downflow and upflow packed-bed reactors over pillared clay catalyst

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## Abstract

An experimental study is presented for comparing the behavior of a packed bed reactor in the catalytic liquid-phase oxidation of aqueous phenol with two modes of operation, downflow and upflow. The operating parameters investigated included temperature, reactor pressure, gas flowrate, liquid hourly space velocity and feed concentration. Because of the completely wetted catalyst, the upflow reactor generally performs better for high pressures and low feed concentrations when the liquid reactant limitation controls the rate. The interaction between the reactor hydrodynamics, mass transfer, and reaction kinetics is discussed. For both operation modes, complete phenol removal and significant total organic carbon (TOC) reduction can be achieved at rather mild conditions of temperature (150–170 °C) and total pressure (1.5–3.2 MPa). The results show that the phenol and TOC conversion are considerably affected by the temperature, while the air pressure only has minor influence. Total elimination of TOC is difficult since acetic acid, as the main intermediate, is resistant to catalytic wet oxidation. All tests were conducted over extrudates of Fe–Al pillared clay catalyst, which is stable and maintains its activity during the long-term experimental process. No significant catalyst deactivation due to metal ion leaching and polymer deposition was detected. © 2004 Elsevier Ltd. All rights reserved.

**Keywords:** Aqueous phenol solution; Catalysis; Multiphase reactors; Packed bed; Reaction engineering; Wet air oxidation

## 1. Introduction

Industry creates large annual amounts of wastewater containing products hazardous to the environment. Among all the organic materials that we are concerned with, phenol is important because of its ever-increasing presence due to its increased production: in 1995, 1900 million kg were produced in the USA alone (Fortuny et al., 1998). Phenol and phenolic substances are used widely as raw materials for organic compounds, such as dyes, pharmaceuticals, plasticizers, and antioxidants. However, phenol, in addition to having a strong disagreeable odor and taste in water even at very small concentrations, is extremely toxic to aquatic life and resistant to biodegradation. At present, several

treatment methods are available: chemical, physical (adsorption, reverse osmosis, etc.), biological, wet air oxidation (WAO), and incineration. In selecting a wastewater treatment process among these methods, one should take into account the toxicities and concentrations of the pollutants in the waste stream.

Chemical oxidation, using  $O_3$ ,  $ClO_2$ ,  $Cl_2$ , and  $H_2O_2$  as oxidants, is a popular method. However, it is prohibitively expensive if large volumes are to be treated, particularly if the waste is predominantly organic. In view of this, chemical treatment is usually used as a pretreatment step for removing color and some toxic compounds so that other treatment methods, such as biological treatment, can be used downstream (Yurii and Moshe, 1998). UV/ $O_3$  oxidation allows the combination of photocatalysts and UV light to achieve higher reaction rates in aqueous streams, but the ozone and UV lighting requirements can be expensive as well as difficult to scale up to industrial sized reactors (Matthews, 1992).

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As a physical treatment method, an adsorptive process over activated carbon (and some synthetic resins) is used frequently to treat wastewater. High-molecular-weight organics (particularly those having lower solubility in water) are adsorbed preferentially on the carbon surface. Carbon adsorption treatment becomes attractive if the spent carbon can be regenerated by biotreatment or solvent extraction. Reverse osmosis is a membrane process used for desalting brackish water and removing dissolved solids from certain industrial wastewaters. However, the technique is not used frequently primarily due to high membrane replacement costs.

Routine biological methods for wastewater cleaning are not effective in the chemical, agricultural, and pulp and paper industries. For example, it is generally difficult to biotreat waste streams having phenols above 200 ppm (Pruden and Le, 1976). In addition, biodegradation processes are inherently slow and do not allow for high degrees of removal. Evidently, specifically designed pre-treatment processes are frequently required to reduce the impact of the toxic organics on the classical activated sludge plants; otherwise, the biodegradation processes fail (Yurii and Moshe, 1998).

Noncatalytic wet oxidation becomes energetically self-sustaining with no auxiliary fuel requirement when the feed chemical oxygen demand (COD) is higher than 30 g/L, while incineration requires more than 300 g COD/L to sustain self-combustion (Imamura, 1999). The contaminated aqueous stream is oxidized by air or oxygen at subcritical conditions at temperatures from 200 to 300 °C and pressures from 70–230 atm (Mishra et al., 1995); the supercritical oxidation process requires even more severe conditions, typically around 500 °C and 270 atm (Ding et al., 1996). At these operating conditions, the reactor is pressurized to prevent the liquid from boiling and evaporating. Due to the required large investment in high-pressure equipment and the high cost of running the reaction at high pressures and temperatures, subcritical or supercritical noncatalytic wet oxidation is rather expensive.

The severity of oxidation conditions can be reduced by use of a suitable (cheap, stable, and resistant to poisoning) catalyst system. Catalytic wet oxidation (CWO) of liquid-phase phenol, which is frequently used as a model substance,

has been performed with many catalytic systems (Table 1). Among the promising materials, Al–Fe pillared clay catalyst has shown encouraging results for oxidizing organic compounds in aqueous media in a slurry reactor in powder form (Barrault et al., 2000) and in a basket stirred tank reactor in extrudate form (Guo and Al-Dahhan, 2003a). This novel catalyst allows for mild conditions and can be used for a rather long time without significant catalyst leaching and deactivation. Therefore, Al–Fe pillared clay catalyst is employed in this work in order to further explore its potential.

After the catalyst is selected, the reactor and process design for the catalytic reaction are also addressed. CWO is usually carried out in trickle-bed reactors, bubble columns, and mechanically agitated reactors, which lead to different reaction phenomena. For instance, formation of phenolic polymers was observed in CWO of phenol using a copper oxide catalyst in slurry reactors (Sadana and Katzer, 1974), whereas no polymers were found when a packed bed reactor was used (Fortuny et al., 1995). The tentative explanation is based on the assumed simultaneous presence of two different reactions for phenol removal: classical oxidation and condensation reactions that form polymers. From a chemical point of view, the very high liquid to solid ratio in the slurry reactor could enhance the formation of heavy polymers through oxidative coupling. These polymers could irreversibly adsorb on the catalyst surface and progressively block the active sites, thereby lowering the rate of phenol removal and preventing further oxidation of intermediate molecules (Pintar and Levec, 1994). Consequently, reactors with high liquid-to-catalyst volumetric ratio (such as a slurry system) should not be used to treat wastewaters containing pollutants that tend to polymerize (Pintar et al., 1997). On the other hand, the oxidation of phenol towards intermediates (aromatic compounds, carboxylic acids) and the end product (carbon dioxide) was experimentally found to be strongly enhanced in the packed bed system (Fortuny et al., 1995). Packed-beds possess a high catalyst-to-liquid ratio, but they require a stable catalyst that is active at moderate temperatures, such as the Al–Fe pillared clay catalyst.

Packed-bed reactors with downflow of gas and liquid phases are widely encountered in industrial practice, while

Table 1  
Studies on CWO of phenol in aqueous solution in packed-bed reactors

Reference	Catalyst	Temp (°C)	Press. (atm)	C <sub>o</sub> (g/L)	Reaction time (min)	Conversion
Imamura et al., 1988	MnO <sub>2</sub> /CeO <sub>2</sub>	220	10	2.0	20	92.7
Pintar and Levec, 1994	CuO-ZnO-CoO	50–210	3–8	0.1–0.5	1	100
Krajnc and Levec, 1994	CuO-ZnO/ cement	380–390	230	5.0	0.25	—
Fortuny et al., 1995	CuO/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	120–160	6–12	5.0	30	80
Ding et al., 1996	Cr <sub>2</sub> O <sub>3</sub> ,V <sub>2</sub> O <sub>5</sub> /Al <sub>2</sub> O <sub>3</sub>	390–410	241	.23–8.4	—	—
Tukac and Hanika, 1998	Active C / Ni, V, Fe	120–160	20–50	5.0	60	100
Zhang and Savage, 1998	MnO <sub>2</sub> /CuO/Al <sub>2</sub> O <sub>3</sub>	380–430	250	0.1	—	—
Fortuny et al., 1999	CuO/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	120–160	30–60	5.0	60	97
Stuber et al., 2001	Active C	140–160	27–38	2.5–5	120	100

different modes of operation, such as gas–liquid upflow, are also becoming important. The principal question is whether a downflow or an upflow mode of operation optimizes the conversion and selectivity. Considering the complicated fluid–fluid and fluid–particle interaction, and the complex geometry of the tortuous pore space, the selection of operation mode is dependent on the characteristics of a specific reaction system. Therefore, in this work, based on the previous basket reactor studies, the performance of the pillared clay catalyst for the continuous CWO of phenol will be tested experimentally in a packed-bed reactor with co-current downflow and upflow. In addition, operating parameters needed for complete mineralization will be identified.

## 2. Experimental

### 2.1. Catalyst materials and product analysis

Al–Fe pillared clay catalyst particles were produced and used in a cylindrical form ( $\phi 2 \times 8$  mm, approximately). Product samples were collected from the reactor outlet stream. The phenol conversion and product distribution were analyzed by high-performance liquid chromatography (HPLC). Total organic carbon (TOC) was detected by a Shimadzu TOC-500 analyzer. Details on characterization of catalyst materials and sample analysis have been reported in a previous work (Guo and Al-Dahhan, 2003b).

### 2.2. Experimental setups and procedures

The configuration of the reactor system, which is shown in Fig. 1, allowed for the isothermal and isobaric conditions.

The reactor was made of  $\phi 2.1 \times 60$  cm stainless steel tubing. The packing material was supported by a stainless steel screen placed near the bottom of the reactor tube. The Fe–Al pillared clay catalyst was packed to a height of 30 cm, with glass beads ( $\phi 3$  mm) packed on the top and bottom sections, and each section had a 15 cm long inert zone. Upon entering the reactor inlet, the liquid and gas reactants were mixed and heated in the inert packing to a preset temperature. Then the heterogeneous reactions took place after the air and liquid contacted the catalyst. The temperature in the reactor was monitored by three thermocouples inserted into the packed bed through side openings evenly spaced along the reactor length. The temperature at each section was controlled using LABVIEW software via a National Instruments SCXI-1325 data acquisition board, which regulated the voltage supplied to the heating tapes wrapped around the reactor sections. Since the phenol feed concentration was low, no temperature rise due to reaction was considered. The temperature value was held constant to within  $\pm 1$  K, which confirms that the reactor was operated isothermally.

The liquid reactant, an aqueous solution of phenol, was loaded in the feed tank and fed to the system at high pressure through a Waters 510 HPLC pump capable of volumetric flow rates up to 10 mL/min with high precision and continuous flow. In order to saturate the gas and prevent solvent evaporation effects, before air entered the reactor it was bubbled through two cylinders containing water. The pressure and flow rate of the gas system was controlled with a high-pressure regulator and the backpressure regulators on the exit of the system.

Liquid and gas were fed to the reactor through stainless steel lines equipped with three-way valves to allow for both

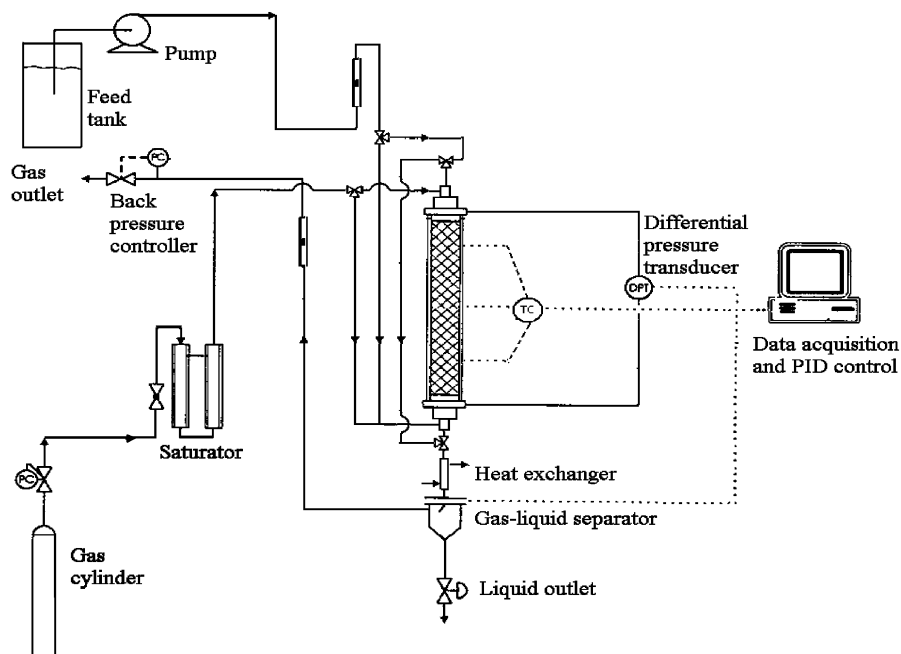


Fig. 1. Experimental setup of a catalytic packed-bed reactor suitable for gas–liquid cocurrent downflow and upflow.

downflow and upflow configurations by merely switching the valve positions. Switching between the two modes of operation without discharge enables performance comparisons at identical catalyst activities. The gas and liquid distributions are critical in downflow operation, while gas distribution is important in upflow operation. The experimental facility was equipped with uniform gas–liquid distributors and control valves for both downflow and upflow operation modes. Distributors were placed at the top and the bottom of the reactor column. If the reactor was in trickle flow configuration, the liquid was channeled into several tubes and flowed out a perforated disk to distribute the liquid evenly over the whole catalyst bed, and the gas entered the space surrounding the tubes. The upflow connection was designed in the form of a U-shaped stainless steel box. Seven holes on top of the box distributed the gas uniformly, while the liquid line is concentric to the gas delivery line and feeds the liquid all around the gas distributor box. The distributors were tested using a clear acrylic reactor to ensure that no channeling effect occurred during operation.

After the mixture exited the reactor and was cooled in a heat exchanger, the reactor effluent was then separated into the gas and liquid phase in a high-pressure separator. The bottom of the separator had a liquid exit controlled either by a micrometric valve or by the liquid level control device. The micrometric valve allowed for sampling of the liquid collected in the separator. The amount of liquid in the separator was adjusted by a level sensor. The liquid control device monitored vibrations in a paddle that extended down into the separator. As the liquid level changed, the frequency of the vibrations of the paddle changed. This change was transformed into a signal that turned on/off the liquid exit valve to maintain the preset liquid level. Abrupt changes in volume of the liquid contained in the separator could cause changes in pressure. The gas stream from the separator was discharged through a back-pressure controller which maintained constant pressure in the reactor. To prewet the packing, before the experiments were started, the reactor was flooded with liquid phase for 10 h, followed by draining.

### 3. Results and discussion

#### 3.1. Selection of operating conditions

Prior to the experimentation in a packed bed reactor, a stirred basket reactor test at different temperatures in the range of 90–170 °C had revealed that phenol conversion becomes significant (> 20%) after 0.5 h and complete mineralization takes place after 4 h. Therefore, in order to get the desired high phenol conversion in the packed bed, the liquid hourly space velocity (LHSV) was chosen to let the liquid residence time range between 0.5 and 5 h, as listed in Table 2.

The operation regime was kept away from spray flow to assure the liquid film dominated the mass transfer resistance (Levenspiel, 1996). Therefore, for the downflow operation,

Table 2  
Selection of design and operating conditions

Property	Range
Temperature, °C	110–210
Equilibrium vapor pressure, MPa	0.14–0.79
Total pressure, MPa	1.5–3.2
Reactor diameter, cm	2.5
Bed height, cm	60
Bed porosity	~ 0.4, ~ 0.6
Catalyst particle size, mm	$\phi 2 \times 8$
LHSV, h <sup>-1</sup>	0.2–2
Superficial gas velocity, cm/s	0.13–2.45
Superficial gas mass flux, kg/m <sup>2</sup> /s	0.03–0.13
Phenol feed concentration, mg/L	500–2000

according to the map of hydrodynamic flow regimes proposed by Fukushima and Kusaka (1977), gas velocity should be low ( $Re_G < 350$ ). For the upflow operation, the hydrodynamic flow regimes proposed by Fukushima and Kusaka (1979) increased the limit ( $Re_G < 800$ ) to avoid spray flow. In addition, the flow map reported by Turpin and Huntington (1967) gave an upper limit for the gas mass velocity (< 0.2 kg/m<sup>2</sup>/s) for the upflow. Therefore, to satisfy the above conditions, the selected gas mass velocity is also listed in Table 2. For the selected liquid and gas mass flux, the resulting ratio of the  $G/L$  molar flow rate falls into the range from 3000 to 10 000, so that an excess of oxygen is supplied to the liquid bulk.

Before conducting experiments over catalysts, the reactor was filled up with inert glass beads. A group of experiments were performed at the severe conditions: 170 °C, 3.2 MPa, and different LHSV. Analysis of liquid-phase samples of the reactor's exit stream revealed that uncatalyzed homogeneous oxidation led to phenol and TOC conversions less than 10%. On the basis of these results, it was verified that the effect of homogeneous oxidation was insignificant. Therefore, we can affirm that reactant concentrations remained unchanged when they passed through the inert glass bead section. In addition, the applied air pressure exceeded the vapor pressure of the liquid phase over the entire range of used temperatures to prevent evaporation inside the bed. Corresponding to the temperature range of 110–170 °C, the equilibrium vapor pressure is from 0.14 to 0.79 MPa (Lin et al., 1996), while the reactor pressure range is 1.5–3.2 MPa.

#### 3.2. Theoretical background

The reaction rate over externally incompletely wetted packing can be smaller or greater than the rate observed over completely wetted packing. This difference depends on whether the limiting reactant is present only in the liquid phase or in both gas and liquid phase. As pointed by Khadilkar et al. (1996), most gas–liquid reaction systems promoted by a solid catalyst can be classified as being liquid reactant or gas reactant limited, which can be delineated by



Table 3  
Identification of the limiting reactant for the packed bed experiments

Temperature °C	Total pressure (MPa)	O <sub>2</sub> Solubility (mol/m <sup>3</sup> )	Diffusion Coefficient <sup>a</sup> [cm <sup>2</sup> /s]		$\gamma^b$	$\gamma^c$
			O <sub>2</sub>	Phenol		
110	1.5	2.125	1.100E–04	4.816E–05	1.57E–01	6.26E–01
110	3.2	4.875	1.100E–04	4.816E–05	6.83E–02	2.73E–01
170	1.5	1.419	1.997E–04	8.743E–05	2.34E–01	9.38E–01
170	3.2	4.943	1.997E–04	8.743E–05	6.73E–02	2.69E–01

<sup>a</sup>Diffusion coefficient calculated from Wilke–Chang method (Wilke and Chang, 1955).

<sup>b</sup>Phenol concentration: 500 ppm.

<sup>c</sup>Phenol concentration: 2000 ppm.

the parameter  $\gamma$ . The ratio of the diffusion fluxes of the two reactants scaled by the ratio of stoichiometric coefficients, ( $\gamma = (D_{eB}C_B)/v_B(D_{eA}C_A^*)$ ), is indicative of the relative availability of the species at the reaction site. The reaction can be considered gas reactant limited for  $\gamma \gg 1$  or liquid reactant limited for  $\gamma < 1$ .

The limiting reactant in a gas-limited reaction can enter the porous particles through both the actively and inactively wetted surfaces, but it enters at different rates. Accordingly, for a gas limited reaction, a trickle-bed reactor is expected to perform better than an upflow reactor, due to its partially wetted catalyst over which gas reactant has an easy access to the particles. In an upflow reactor, the only access of the gaseous reactant to the catalyst is through the liquid film engulfing the catalyst. For a liquid-limited reaction, the liquid reactant can enter the catalyst particle only through its actively wetted surface, leaving the inactively wetted areas unutilized. Since upflow has higher external wetting efficiency (100%) than downflow, it will facilitate the transport of the liquid reactant to the catalyst and enhance the reaction rate. Liquid reactant limited conditions, therefore, result in a better performance for upflow, where particles are completely surrounded by liquid, than for downflow, where particles may be only partially externally wetted.

In this work, oxygen is not very soluble in water, and phenol is also present in low concentration. Based on the employed operating conditions, the resulting ratio of the diffusion fluxes of the two reactants are listed in Table 3, where only the highest and lowest temperatures and pressures are chosen to estimate the range of  $\gamma$  values. Because all the values of  $\gamma$  are less than unity ( $\gamma < 1$ ), the studied CWO reactions are liquid reactant limited. Hence, it is expected that the upflow will allow the catalyst to achieve better reactant conversion. However, such a theoretical expectation still needs experimental verification.

### 3.3. Comparison of the performance of trickle-bed and upflow reactors

Knowledge of flow regime is indispensable in the analysis of downflow and upflow packed bed performance. In a

trickle-bed reactor, at low gas and liquid flow rates, the flow regime is characterized by a continuous gas phase and some discontinuous liquid films driven by gravity force. While in an upflow packed bed reactor, the buoyancy force leads to a bubble flow regime with a continuous liquid phase which contains small spherical bubbles. In this regime, the solid particles are fully wetted by the continuous liquid phase.

The differences in downflow and upflow modes give rise to varied liquid holdup, external catalyst wetting, axial dispersion, wall effects, and maldistribution, which in turn affect the chemical reaction process. Actually, it has been suggested that the phenol liquid–solid mass transfer coefficient values do not differ much for the two modes of operation, if everything else is kept identical (Iliuta and Larachi, 2001). Moreover, the relative difference between the overall effectiveness factor for a partially wetted catalyst pellet and a fully wetted catalyst particle has been found not to exceed 8% (Iliuta and Larachi, 2001). To correctly understand the underlying aspects that are responsible for the reactor performance, it is necessary to study the operating parameters individually.

#### 3.3.1. Effect of liquid velocity

One comparison of the two reactors is achieved by studying the conversion at identical LHSV (defined as superficial liquid velocity/reactor length) and identical reactant feed concentration. LHSV is the proper scale-up variable when the beds for downflow and upflow are identically packed and the reaction rate is based per unit volume of the catalyst. For gas-limited reactions, scale-up at constant LHSV can lead to very poor performance as the catalyst effectiveness factor drops with increased contacting efficiency due to a reduction in the gas reactant supply. Hence, for gas-limited reactions, constant LHSV and constant reactor height are required in order to maintain the same performance upon scale-up. However, since the CWO reaction covered in this work is liquid limited, scale-up at constant LHSV is forgiving since it results in improved wetting efficiency and better catalyst utilization (Dudukovic et al., 1999).

In laboratory scale packed beds, because low liquid velocity is frequently used in order to match the LHSV of

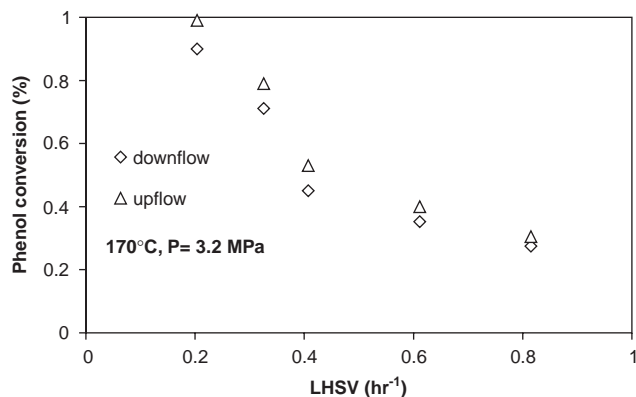


Fig. 2. Trickle-bed ( $Pe_l = 21\text{--}33$ ) and upflow ( $Pe_l = 3\text{--}4$ ) performance at different LHSV (Pressure = 3.2 MPa, [phenol] = 500 ppm, and  $U_g = 0.28$  cm/s).

the commercial unit, most of the downflow cases can be classified in the trickle flow regime. Similar liquid and gas flowrates were also applied to the upflow operation, using the same bed voidage. The effect of LHSV on phenol removal rate is presented in Fig. 2.

For both operation modes, phenol conversion decreases with the increased liquid mass velocity, at a pressure of 3.2 MPa and a temperature of 170 °C. The effect of liquid superficial velocity on the axial phenol conversion profile is obvious. A lower feed flow rate is preferred because the longer residence time will allow for complete phenol removal. A similar trend of results can be obtained in the cocurrent upflow packed-bed reactor where gas flows through the liquid in bubble flow. Although a high liquid superficial velocity enhances the mass transfer coefficient, it actually lowers the liquid reactant residence time, which corresponds to the decreased exit conversion.

It is evident that phenol conversion values were higher in the upflow system than in the downflow system. The differences between these two modes became more noticeable at lower LHSV. Liquid axial dispersion was calculated based on the correlations proposed by Cassanello et al. (1992). As shown by the reactor scale liquid Péclet number, for the same set of operating conditions, liquid backmixing is more prominent in the upflow configuration than in the down flow configuration, which is not beneficial for phenol conversion. However, in the downflow reactor, incomplete catalyst utilization may occur. One cause is reactor scale liquid maldistribution that may leave certain portions of the bed poorly irrigated. The other cause is particle scale incomplete external wetting: at sufficiently low liquid mass velocity, the liquid flow available is insufficient to cover all the catalyst particles with a continuous liquid film at all times. In a time-averaged sense, the external surface of the particle is then only partially covered by the flowing liquid. In a liquid limited reaction, the conversion will be governed by the degree of catalyst wetting. Since downflow operation results in regions of poorly wetted catalyst, upflow has higher wetting

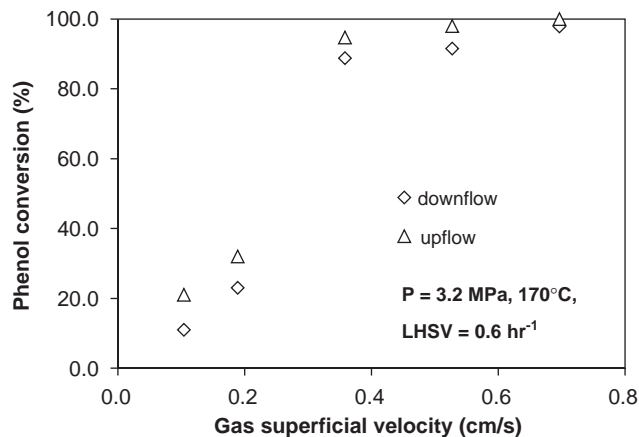


Fig. 3. Effect of gas velocity on phenol conversion at downflow ( $Pe_l = 31$ ) and upflow ( $Pe_l = 4$ ) reactor.

(100%) than downflow and it will outperform downflow. As the liquid flowrate increases (i.e., space time is decreased), the wetting efficiency of the trickle-bed reactor is greatly enhanced, and its performance approaches that of upflow reactor, as shown in Fig. 2. Therefore, catalyst wetting efficiency is one essential factor affecting a laboratory reactor's performance.

### 3.3.2. Effect of the gas velocity

Fig. 3 shows that the phenol conversion at a given LHSV was enhanced by increasing the gas velocity for both modes of operation at high reactor pressure. The conversion was found to increase almost linearly with an increase in the air velocity. The strong dependence was due to a linear increase in the gas–liquid and liquid–solid mass transfer coefficients with the gas velocity (Stuber et al., 1996). However, the effect of gas velocity on reactor performance diminished when gas velocities became moderate.

Both Figs. 2 and 3 reveal that the reactor performance was distinct for different flow direction when the fluid (liquid or gas) flowrate was low, while this distinction vanished at elevated flowrates. At low gas velocities, gravity (or buoyancy) force plays an important role. The flow regime was bubble flow in upflow and trickle flow in downflow, which created distinct hydrodynamics and reaction processes. However, when the flowrates of liquid and gas increased, the flow approached pulsing flow in both directions. The hydrodynamic characteristics were mainly governed by inertial force, and the flow direction does not play a role any more.

At high pressure and low feed concentration of phenol, the reaction is liquid limited. In this case upflow performed better than down flow, although the former leads to higher liquid axial dispersion (lower Péclet number), as shown in Fig. 3. In downflow operation, the catalyst articles are not fully wetted at the liquid flow rates used, which facilitates the access of the gas reactant to the pores of the catalyst from the externally dry parts. However, the availability of gaseous reactant was not a dominant factor in this case. The

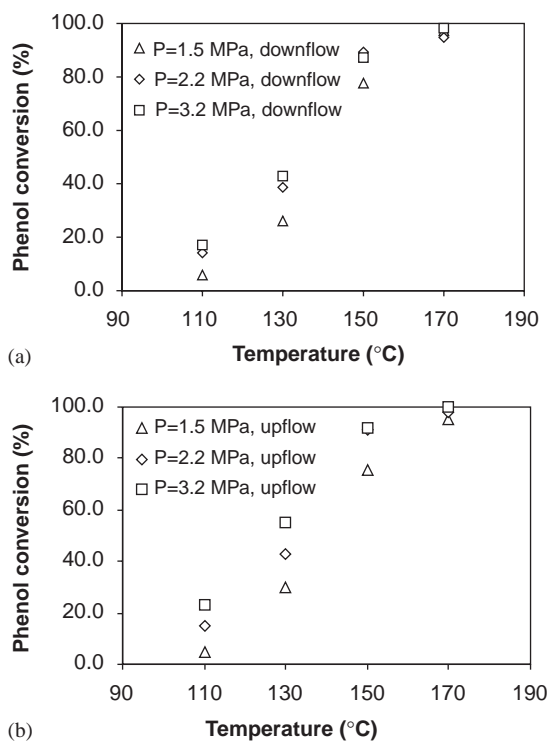


Fig. 4. Effect of air pressure on phenol conversion at downflow ( $Pe_I = 24$ ) and upflow ( $Pe_I = 3$ ) reactor. (LHSV =  $0.3 \text{ h}^{-1}$ , [phenol] = 500 ppm,  $U_g = 0.53 \text{ cm/s}$ ).

access of the reactant to the catalyst site was limited by the surrounding liquid film only.

At a given pressure and liquid mass flow rate, the liquid holdup decreased when the gas mass flow rate was increased. An abrupt decrease was observed at low gas flow rates, followed by a slight decrease at higher gas flow rates. Such trends have been confirmed regardless of the flow direction and the pressure (Larachi et al., 1991). In addition, the dimensionless pressure gradient ( $\Delta P / \rho_L g Z$ ) increases significantly and so does the shear stress on the gas–liquid interface (Al-Dahhan and Dudukovic, 1995). Therefore, liquid film thickness at a constant liquid flow rate decreases, which leads to a better spreading of the liquid film over the external packing area and across the reactor diameter. Accordingly, the catalyst wetting efficiency and gas–liquid interfacial area improved considerably, which is supported by the finding of Larachi et al. (1992). Since the trickle-bed pellets get progressively entirely wetted by increasing the gas superficial velocity, the difference in the performances by the two modes of reactor operation narrows, and the downflow performance approaches that of upflow.

### 3.3.3. Effect of reactor pressure

Fig. 4 shows that the effects of increasing gas pressure on phenol disappearance rate. A significant improvement in phenol conversion occurred when pressure changed from 1.5 to 2.2 MPa as compared to the change in conversion

when pressure changed from 2.2 to 3.2 MPa. This finding implies that the effect of pressure diminishes when pressure becomes high, because the reaction becomes liquid reactant limited at low feed concentrations of phenol (500 ppm) and high pressure ( $> 1.5 \text{ MPa}$ ). Further increase in the reactor pressure, and hence liquid phase oxygen concentration, will have a minimal effect since oxygen is not the limiting reactant anymore.

Elevated levels of pressure and temperature improve the solubility of oxygen (Himmelblau, 1960). This in turn increases the mass transfer driving force for gas to the inactive wetted catalyst surface in the downflow mode, and facilitates the rate of mass transport to the wetted catalyst surface in both modes. Below a critical value of superficial gas velocity ( $\approx 1 \text{ cm/s}$ ), the elevated pressure causes a decrease in liquid holdup and an increase in catalyst wetting efficiency, but in a less pronounced manner since the pressure gradient is more sensitive to velocity changes than to gas density (Al-Dahhan and Dudukovic, 1995). In addition, neither of the two mass-transfer parameters, the interfacial areas and the liquid-side volumetric mass-transfer coefficients, depends on pressure (gas density) (Al-Dahhan et al., 1997). However, for gas velocities larger than 1–2 cm/s, pressure intensifies the gas shear over the trickling liquid films. The reactor flow regime shifts from a state predominantly controlled by gravity (trickle flow with low gas flow rate) to a state controlled by gas–liquid shear stress (Wammes et al., 1990). The gas–liquid interfacial area also increases at elevated pressure. Due to shear intensification, the liquid trickle films are invaded by tiny bubbles whose size results from a balance between viscosity and surface tension forces. It is the formation of such small bubbles that enhances the interfacial area and the volumetric mass-transfer coefficient (Al-Dahhan et al., 1997). Hence, due to the enhanced gas–liquid interaction and interphase mass transfer, an increased gas pressure is favorable for the performance of both upflow and downflow reactors.

At higher pressure, since the  $\gamma$ -ratio will diminish faster than the increase in wetting efficiency in downflow, it is expected that an upflow operation will remain more favorable for conducting CWO than downflow operation. From the aforementioned experimental observations, it is stressed that the experimental performance of these reactors becomes similar at high liquid mass velocities, high pressure, or high gas velocity when the catalyst in the trickle-bed reactor becomes completely wetted, as usually encountered in the upflow reactor.

### 3.3.4. Effect of reactor temperature

The increased phenol removal rate at higher temperature is also shown in Fig. 4. The doubled gas pressure enhanced the phenol conversion only to within 20%, while a temperature increment of  $80^\circ\text{C}$  resulted in an evident enhancement (up to 90%) of the phenol conversion. Therefore, having more pronounced effect, temperature is a key factor

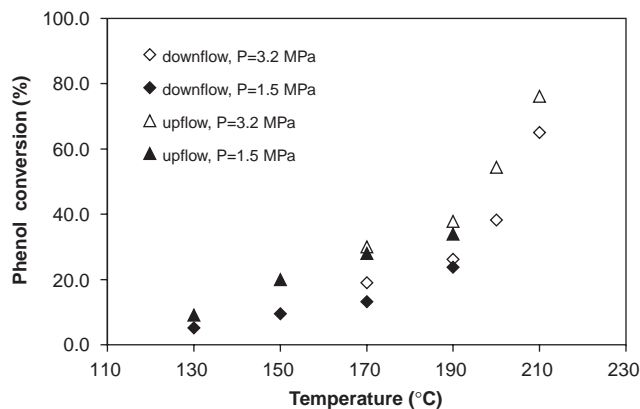


Fig. 5. Trickle-bed ( $P_{el} = 24$ ) and upflow ( $P_{el} = 3$ ) performance at different reaction temperatures (LHSV =  $0.3 \text{ h}^{-1}$ ,  $U_g = 0.13 \text{ cm/s}$ , [phenol] = 500 ppm).

controlling the reaction rate in the catalytic oxidation. To confirm the distinct effect of temperature and seek an optimum range of operating conditions, more tests were performed by choosing various liquid and gas velocities.

Fig. 5 illustrates temperature's impact at a low gas velocity of  $0.13 \text{ cm/s}$ . The effect of the temperature became weaker, and the conversion can reach only 70–80% at  $210^\circ\text{C}$ . This is in contrast to Fig. 4, where complete phenol conversion can be obtained around  $190^\circ\text{C}$  at a gas velocity of  $0.53 \text{ cm/s}$ . Hence, when low gas velocity was employed, the oxidation reaction was limited by external mass transfer of the gas reactant, which is in agreement with the observed effect of the gas velocity on phenol conversion. Usually, temperature above  $210^\circ\text{C}$  is not desirable in the wet oxidation process because high temperature requires a high reactor pressure to minimize the vaporization of liquid phase. To reduce the reaction's severity, i.e., temperature, moderate gas velocity ( $> 0.5 \text{ cm/s}$ ) is necessary.

The effect of temperature on phenol conversion in the range of  $110\text{--}170^\circ\text{C}$  for LHSV between  $0.3$  and  $1.2 \text{ h}^{-1}$  is depicted in Figs. 6a and b, for downflow and upflow operation mode, respectively. The experimental data confirms that the reaction rates can be satisfying at a moderate gas velocity of  $0.53 \text{ cm/s}$  and low liquid velocity. When the reactant stays in the reactor for a rather long time, the temperature effect is dominant over the mass transfer effect, and the system is under chemical kinetic control. In particular, a temperature change from  $150$  to  $170^\circ\text{C}$  led to an obvious acceleration of the reaction rate. High temperature is especially beneficial for the upflow mode, where flow maldistribution can be minimized.

### 3.3.5. Effect of feed concentration

Since the catalyst was found active in the previous studies with moderate phenol loading (500 ppm), the CWO process was further tested with phenol solution in rather high concentrations (1000 and 2000 ppm), simulating industrial applications. The results, presented in Figs. 7a and b, show

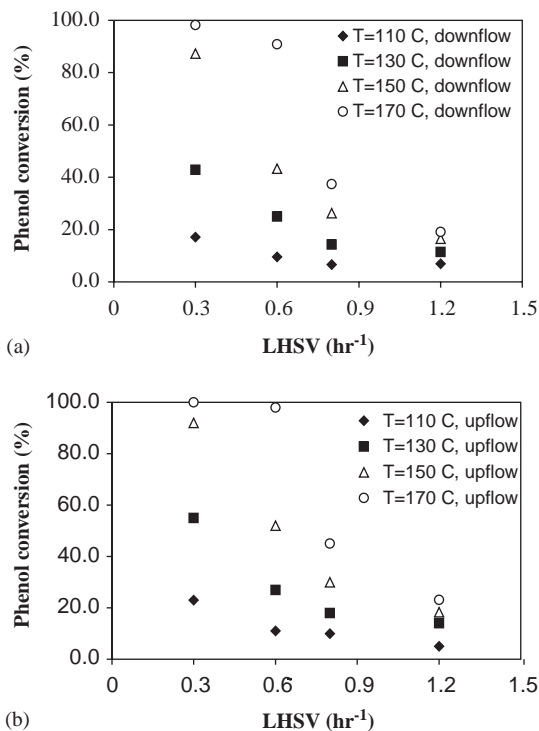


Fig. 6. Phenol conversions at different LHSV and reaction temperatures for downflow ( $P_{el} = 24\text{--}39$ ) and upflow ( $P_{el} = 3\text{--}5$ ) packed-bed reactors (Pressure = 3.2 MPa,  $U_g = 0.53 \text{ cm/s}$ , [phenol] = 500 ppm).

that the difference among phenol reductions in the employed three concentrations was not significant. In fact, even for the solution with phenol loading of 2000 ppm, the final conversion still reached above 90% at  $170^\circ\text{C}$ . A similar observation was reported by Stuber et al. (2001), where almost complete phenol elimination was achieved over active carbon catalyst for an initial phenol concentration of 2500 ppm. The reaction kinetics for catalytic air oxidation of phenol are shown in Eq. (1) (Guo and Al-Dahhan, 2003a).

$$r_H = \frac{k_1 K_{\text{PHOH}} K_{\text{O}_2}^{0.5} C_{\text{PHOH}} C_{\text{O}_2}^{0.5}}{1 + K_{\text{PHOH}} C_{\text{PHOH}}} \quad (1)$$

When phenol concentration  $C_{\text{PHOH}}$  is low, the product of the phenol adsorption constant,  $K_{\text{PHOH}}$  and the phenol concentration  $C_{\text{PHOH}}$  will be fairly small compared to 1 in the denominator. In this case, it is reasonable to state that the oxidation rate is approximately first-order with respect to phenol. On the other hand, when phenol concentration  $C_{\text{PHOH}}$  increases so that the value of  $K_{\text{PHOH}} C_{\text{PHOH}}$  becomes dominant in the denominator, the reaction of phenol oxidation will approach a zero-order reaction with respect to phenol.

The shift in reaction kinetics due to feed concentration change was confirmed by experimental data at high pressure (3.2 MPa) for both downflow and upflow operation mode, as shown in Figs. 7a and b. Conversion was independent of feed concentration at low phenol loading, which is the indicative of a first-order reaction due to the phenol transport



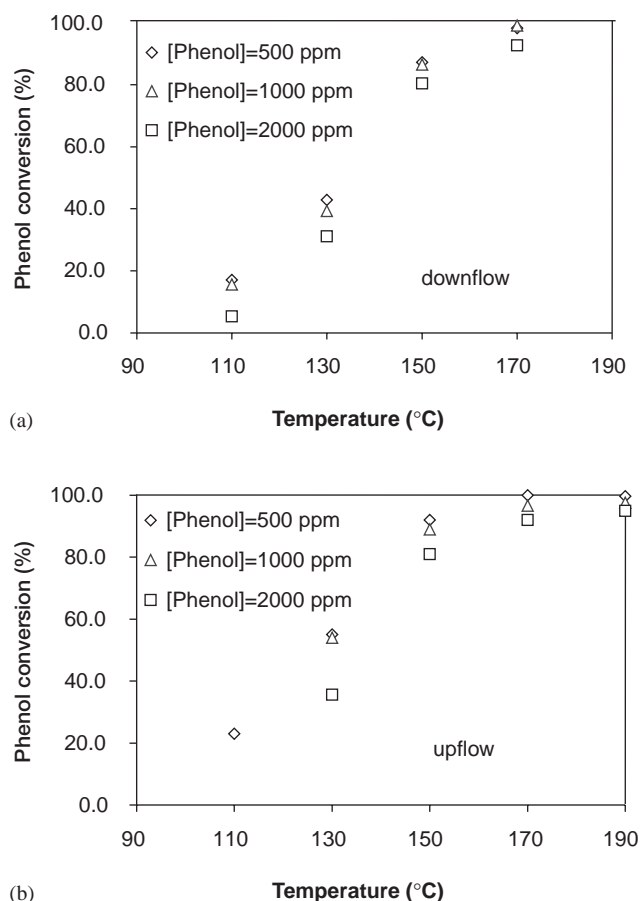


Fig. 7. Phenol conversion at different phenol inlet concentrations for downflow ( $Pe_l = 24$ ) and upflow ( $Pe_l = 3$ ) (Pressure = 3.2 MPa, LHSV =  $0.3 \text{ h}^{-1}$ ,  $U_g = 0.53 \text{ cm/s}$ ).

limit. As the phenol concentration became high, the first-order dependence vanished and zero-order dependence was noticed. An inverse proportionality of conversion with liquid reactant feed concentration (typical of zero-order behavior) was observed, especially at low temperature where the value of phenol adsorption constant  $K_{\text{PHOH}}$  was small.

Shown in Figs. 7a and b, comparisons can be made between phenol overall conversions in the trickle bed and the upflow reactor for different inlet concentrations. Under the same test conditions, liquid back-mixing was more significant in the upflow reactor than in the trickle bed, but the former outperforms the latter regardless of the feed phenol concentration. Similar phenomena were reported for other liquid-limited reactions, such as ethanol oxidation (Goto and Mabuchi, 1984).

### 3.3.6. Catalytic wet oxidation of TOC

In the previous work conducted in a stirred tank reactor, the main detected intermediates in the product effluent were acetic acid, catechol, and hydroquinone. Oxalic acid and benzoquinone were also identified in measurable quantities (Guo and Al-Dahhan, 2003b). However, once the cat-

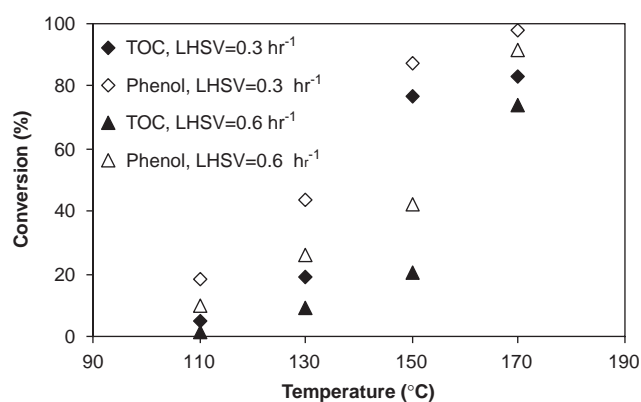


Fig. 8. TOC and phenol conversions obtained in a trickle-bed reactor as a function of temperature (LHSV =  $0.3 \text{ h}^{-1}$  and  $0.6 \text{ h}^{-1}$ , Pressure = 3.2 MPa,  $U_g = 0.53 \text{ cm/s}$ ).

alytic oxidation process occurred in the packed bed reactor, the main detected intermediates were acetic acid and oxalic acid, while catechol and hydroquinone in low amounts were identified as the remaining intermediates. In addition, the pH value of the aqueous solution at the reactor exit decreased considerably, thus suggesting that low-molecular-weight carboxylic acids were produced to an appreciable extent.

Fig. 8 plots TOC conversion against temperature at different LHSV and constant air pressure. It is evident that a gap exists between the TOC conversion values obtained in varied LHSV. This gap is narrow at low temperatures, where the reaction rate is rather low. However, the difference due to the varied LHSV becomes significant when the temperature increases. For low LHSV of  $0.3 \text{ h}^{-1}$ , a temperature increase from 130 to  $150^\circ\text{C}$  enhanced TOC conversion from 20 to 77%, while TOC removal was barely increased for the high LHSV of  $0.6 \text{ h}^{-1}$ . The low flow rates allow the reactants a long time to contact the catalyst surface, where the reaction rate takes place. However, such a trend did not continue from 150 to  $170^\circ\text{C}$ . Although this further temperature increment of  $20^\circ\text{C}$  resulted in expedited reaction rates and noticeable TOC conversion for LHSV of  $0.6 \text{ h}^{-1}$ , TOC removal was scarcely affected by increasing the temperature for LHSV of  $0.3 \text{ h}^{-1}$ . For low LHSV and the resulting long reaction periods, TOC reduction reached a final stage that always involved a certain amount of organics refractory to the catalytic oxidation. The complete TOC mineralization would require that the operating temperatures be increased quite considerably.

There is a substantial difference between TOC and phenol conversion at low temperature (less than  $150^\circ\text{C}$ ), which is indicative of the large amount of partially oxidized products present in the liquid effluent. At  $170^\circ\text{C}$ , it is clear that TOC conversion rate is very close to the phenol conversion rate, which means that during the reaction small amounts of intermediates accumulated in the liquid phase. For the low liquid flowrate, HPLC analysis revealed that the

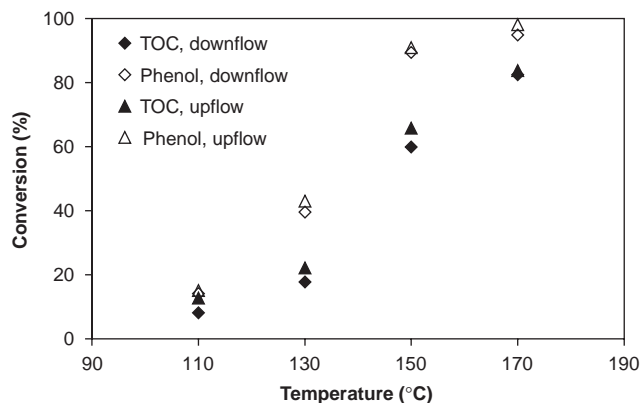


Fig. 9. Effect of flow directions on TOC and phenol conversion, downflow ( $Pe_l = 24$ ) and upflow ( $Pe_l = 3$ ). (LHSV =  $0.3 \text{ h}^{-1}$ , Pressure = 2.2 MPa,  $U_g = 0.53 \text{ cm/s}$ ).

quinone-like products accounted for about 10% of the intermediates detected in the liquid phase. When the flow rate was increased, the liquid residence time decreased, and the percentage of the quinone-like products increased up to 20% of the intermediates detected. As demonstrated by the existence of a maximum at the different residence times tested, these quinone-like intermediates are identified as first stages in the phenol oxidation mechanism and tend to degrade into low-molecular-weight acids. Unlike the quinone-like intermediates, the acetic acid and oxalic acid concentration did not show any maximum, thus indicating that they were refractory compounds in the complex phenol oxidation network.

The experiments conducted at different reaction temperatures with different flow directions also revealed their effects on the TOC reduction, as presented in Fig. 9. In general, TOC and phenol conversion values were higher in upflow than downflow, while the corresponding gap that resulted from the different flow directions is quite narrow. Even though the effects of external mass transfer and diffusion are different in upflow and downflow, they were not the dominant factors. The major dependence of conversion values on temperature demonstrates that the process is controlled by reaction kinetics.

Both Figs. 8 and 9 show that the TOC conversion increased as the operating conditions became more severe, which favors the oxidation of the intermediates, removing them from the exit solution. The small difference between phenol and TOC conversions suggests that the removal rate of phenol and nearly all intermediates are likely to be controlled by the same surface reaction steps. These reaction steps were not limited by benzene ring cleavage, which falls in line with the observations by Pintar and Levec (1994), who reported that the disappearance rates of 1,4-benzenediol and 1,4-benzoquinone are one order of magnitude greater than that of phenol. In addition, the accumulation of short chain carboxylic acids during the oxidation of phenol seems inevitable at low temperatures, since little TOC removal has

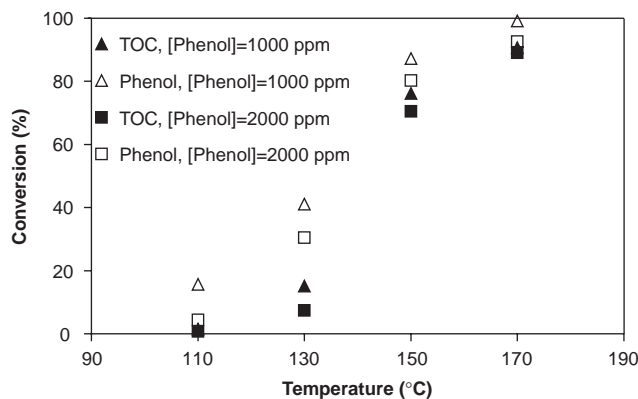


Fig. 10. TOC conversion for different phenol inlet concentrations in a trickle-bed reactor (LHSV =  $0.3 \text{ h}^{-1}$ , Pressure = 3.2 MPa,  $U_g = 0.53 \text{ cm/s}$ ).

been observed under these conditions. It is well known that compounds such as acetic acid, oxalic acid, and other lower carboxylic acids are very resistant to total oxidation even under severe conditions, and their mineralization to carbon dioxide is usually the rate-limiting step in a wet oxidation process (Imamura, 1999).

The results presented in Fig. 10 show that the TOC degradation rate for the selected 1000 ppm phenol inlet concentration was higher than the one for 2000 ppm phenol input, and yet the difference is not significant for all the temperatures tested. For both the selected feed concentrations, the high temperature ( $170^\circ\text{C}$ ) allowed for conversions above 90% for phenol and TOC, respectively, proving that this catalyst is still active at industrial high concentration levels. A similar phenomenon was observed by Silva et al. (2003), who studied CWO of formaldehyde on Mn/Ce catalyst and reported that high TOC reduction ( $> 90\%$ ) can be achieved for different formaldehyde concentrations (800 and 1500 ppm).

It is worthwhile to emphasize that using Fe–Al pillared clay catalysts in the CWO process for a rather high pollutant loading enables a significant TOC reduction. The treated effluent is suitable for further microorganism digestion, so a post-biological treatment can be used as a complement to the CWO reaction process. If intensified energy input is possible (i.e., high temperature and high air flowrate), the Fe–Al pillared clay catalyst can assist the CWO process to achieve the required TOC removal for the direct discharge of wastewaters containing phenol into the environment.

### 3.3.7. Stability of the catalyst

In the reaction process, there is competition between the classical oxidation reaction and the condensation reaction that forms polymers. The polymers, if formed, could irreversibly adsorb on the catalyst surface and progressively block the active site, thereby lowering the rate of phenol removal. However, in the period of 200 h during which data were collected at various operating conditions, the physical blockage of active sites exhibited no considerable influence on the catalytic activity for phenol removal. Moreover,

energy dispersion spectroscopy (EDS) analysis performed at the end of each test identified no carbon polymers deposited on the catalysts. The packed bed preventing condensation products from being formed is in a good agreement with the observations of Pintar et al. (1997), who studied catalytic wet air oxidation of phenol on a catalyst composed of copper, zinc, and cobalt oxides.

In addition, liquid samples were collected every 4 h at the reactor exit and analyzed by the inductively coupled plasma (ICP). The analysis revealed no significant dissolution of the active ion ( $< 0.4$  ppm Aluminum and  $< 0.2$  ppm Iron). The pH of the feed solution was acidic (pH = 4.0), and the most prevalent oxidation products are low-molecular-weight acid, which enhance the acidity of the solution. Even though the reacting medium is acidic and the operating temperature could be high, the low ion leaching shows a strong interaction between the metal elements and the pillars, which stabilizes the active sites of the catalysts.

#### 4. Conclusion

The catalytic liquid-phase oxidation of aqueous phenol solution, conducted in a packed bed reactor with cocurrent downflow or upflow over Fe–Al pillared clay catalyst, revealed that phenol and TOC can be mineralized at relatively mild operating conditions (170 °C and 3.2 MPa). The reactor effluent was almost free of toxic organics, and a biodegradation process may be used as a subsidiary treatment method. Comparisons have been made between the performance of trickle flow (partially wetted catalyst) and upflow packed-bed reactor (completely wetted catalyst). The reaction was found to be liquid-limited at high pressure and low phenol feed concentrations, but it approached gas-limited at low pressure and high feed concentrations of phenol. The upflow reactor performed better at high pressure when liquid reactant limitation controls the rate, due to the completely wetted catalyst in the upflow reactor. The behavior of the downflow and upflow packed-bed reactors was shown to be the result of the interaction of reaction kinetics, mass-transfer phenomena, and reactor hydrodynamics. Reactor temperature, air velocity, and liquid velocity have to be considered as key parameters for tuning the reactor performance. The oxidation of phenol towards the carboxylic acids was found to be strongly enhanced in the packed bed reactor. The dissolution of active metal ions from the catalyst and polymer blockage on the catalyst active site were insignificant. The developed CWO process was used to treat a rather high phenol concentration (2000 ppm) over the Al–Fe pillared clay catalysts. The results showed significant phenol abatement and high TOC reduction. Therefore, this process is potentially promising for industrial wastewaters containing phenol.

#### Notation

$C_i$ , concentration of species  $i$  in liquid phase

$D_e$  effective diffusivity of the reactant,  $m^2/s$   
 $k_1$  heterogeneous reaction rate constant,  $mol\ C/kg/min$   
 $K$  adsorption equilibrium constant,  $m^3/mol$   
 $P$  reactor pressure, MPa  
 $Pe_l$  reactor scale liquid Péclet number  
 $r_H$  heterogeneous reaction rate,  $mol\ C/kg/min$   
 TOC total organic carbon,  $mol\ C/m^3$  solution

#### Sub/superscripts

\* equilibrium  
 A gas reactant,  $O_2$   
 B reactant in liquid phase, phenol  
 G gas phase  
 L liquid phase

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